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<b>(21) International Application Number:</b> PCT/US93/12426 <b>(22) International Filing Date:</b> 20 December 1993 (20.12.93)  <b>(30) Priority Data:</b> 07/997,982      28 December 1992 (28.12.92)      US  <b>(71) Applicant:</b> CHEVRON RESEARCH AND TECHNOLOGY COMPANY [US/US]; P.O. Box 7141, San Francisco, CA 94120-7141 (US). <b>(72) Inventor:</b> CHERPECK, Richard, E.; 8962 Cypress Avenue, Cotati, CA 94931 (US). <b>(74) Agents:</b> CAROLI, Claude, J. et al.; Chevron Corporation, Law Department, P.O. Box 7141, San Francisco, CA 94120-7141 (US).		<b>(81) Designated States:</b> AU, BR, CA, JP, KR, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> PROCESS FOR THE PREPARATION OF POLYISOBUTYL HYDROXYAROMATICS  <b>(57) Abstract</b>  A process for the preparation of a polyisobutyl hydroxyaromatic compound which comprises alkylating a hydroxyaromatic compound in the presence of an acidic alkylation catalyst with a polyisobutene having a number average molecular weight in the range of about 300 to 5,000 and wherein the polyisobutene contains at least about 70 % of a methylvinylidene isomer.		

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-1-

01 PROCESS FOR THE PREPARATION OF POLYISOBUTYL HYDROXYAROMATICS

02

03

BACKGROUND OF THE INVENTION

04

05 This invention relates to a process for the preparation of  
06 polyisobutyl hydroxyaromatics. More particularly, this  
07 invention relates to a process for the preparation of  
08 polyisobutyl hydroxyaromatics which comprises alkylating a  
09 hydroxyaromatic compound with a polyisobutene having a  
10 methylvinylidene isomer content of at least about 70%.

11

12 Alkylation of hydroxyaromatic compounds with polymeric  
13 olefins using acidic catalysts to generate alkylphenols is  
14 well known in the art. However, use of the acidic catalysts  
15 required for the alkylation reaction gives rise to  
16 concurrent polymer degradation and fragmentation of the  
17 polymeric alkyl substituent on the hydroxyaromatic compound.  
18 Known acidic alkylation catalysts have various fragmenting  
19 effects depending on the size of the alkylating agent. Most  
20 catalysts have little effect on olefin alkylating agents of  
21 up to about 20 carbon atoms, that is, having a number  
22 average molecular weight of up to about 280, but severe  
23 fragmentation occurs where alkylating agents of higher  
24 molecular weights are used. Polymeric alkylating agents are  
25 usually derived from propylene or butene and those comprised  
26 primarily of polybutene are the most susceptible to  
27 fragmentation during the alkylation reaction. When  
28 polybutenes having a number average molecular weight of 300  
29 or greater are used, molecular weight degradation of either  
30 the olefin polymer or the substituted alkyl group occurs.

31

32 British Patent No. 1,159,368 discloses that fragmentation of  
33 both the alkylating agent and alkyl substituent can be  
34 reduced but not eliminated by the use of certain specified

-2-

01 reaction conditions. These conditions include the use of  
02 boron trifluoride-phenolate as the acidic catalyst and a  
03 temperature range of 0°C to 65°C, with 0.1 to 1.1 moles of  
04 boron trifluoride and 1 to 4 moles of phenol per mole of  
05 mono-olefinic polymeric alkylating agent having a molecular  
06 weight of 700 to 300,000. Under these conditions, the  
07 fragmentation of polybutene can still only be restricted at  
08 best to a level of about a 10% reduction of average  
09 molecular weight.

10

11 U.S. Patent No. 4,238,628 to Cahill et al. discloses a  
12 process to reduce the molecular weight degradation during  
13 the alkylation of benzene, phenol and naphthol which  
14 comprises alkylating the aromatic compound in the presence  
15 of a boron trifluoride catalyst with a C<sub>3</sub> or higher olefin  
16 polymer having terminal ethylene units.

17

18 According to the Cahill et al. process, the olefin polymer,  
19 preferably polybutene, is first reacted with ethylene to  
20 provide a polymer having terminal ethylene units. The  
21 polymer having such terminal ethylene units is then reacted  
22 with the aromatic compound under alkylating conditions.  
23 Cahill et al. teach that the olefin structure of the  
24 starting polybutene is predominantly the trisubstituted type  
25 with only minor amounts of vinylidene and terminal vinyl  
26 structures present.

27

28 Cahill et al. further teach that polyalkylphenols prepared  
29 with the use of polybutene without terminal ethylene units  
30 undergo molecular weight degradation due to the concurrent  
31 depolymerization reaction. Although the process disclosed  
32 in Cahill et al. results in a reduction in polymer  
33 degradation, the yield of the desired alkylaromatic product

34

- 3 -

01 is not enhanced. In fact, the yield of alkylphenol reported  
02 by Cahill et al. ranged from about 44% to 64%.

03

04 Accordingly, there exists a need in the art for a  
05 hydroxyaromatic alkylation process which minimizes or  
06 eliminates molecular weight degradation while maintaining a  
07 high yield of the desired alkylaromatic product.

08

09

#### SUMMARY OF THE INVENTION

10

11 The present invention provides a novel process for the  
12 preparation of a polyisobutyl hydroxyaromatic compound which  
13 comprises alkylating a hydroxyaromatic compound in the  
14 presence of an acidic alkylation catalyst with a  
15 polyisobutene having a number average molecular weight in  
16 the range of about 300 to 5,000 and wherein the  
17 polyisobutene contains at least about 70% of a  
18 methylvinylidene isomer.

19

20 Among other factors, the present invention is based on the  
21 surprising discovery that hydroxyaromatic compounds can be  
22 effectively alkylated with a high molecular weight  
23 polyisobutene under acid-catalyzed reaction conditions in  
24 significantly high yield, while minimizing or substantially  
25 eliminating molecular weight degradation of the starting  
26 polyisobutene and the resulting polyisobutyl  
27 hydroxyaromatic, by employing a polyisobutene which contains  
28 a methylvinylidene isomer content of at least about 70%.  
29 Moreover, when the hydroxyaromatic compound is phenol, the  
30 resulting polyisobutyl phenol exhibits a high degree of para  
31 substitution, particularly when compared to alkylphenols  
32 prepared from conventional polybutenes having a low methyl  
33 vinylidene content.

34

DETAILED DESCRIPTION OF THE INVENTION

01

02

03 As noted above, the present invention provides polyisobutyl  
04 hydroxyaromatic compounds by a process which comprises  
05 alkylating a hydroxyaromatic compound in the presence of an  
06 acidic alkylation catalyst with a polyisobutene having a  
07 number average molecular of about 300 to 5,000 and a  
08 methylvinylidene isomer content of at least about 70%.

09

10 In general, the polyisobutyl substituent on the polyisobutyl  
11 hydroxyaromatic compound will have a number average  
12 molecular weight in the range of about 300 to 5,000,  
13 preferably in the range of about 400 to 3,000, and more  
14 preferably in the range of about 500 to 2,000.

15

16 The hydroxyaromatic compounds which may be alkylated in  
17 accordance with the process of the present invention include  
18 mononuclear monohydroxy and polyhydroxy aromatic  
19 hydrocarbons having 1 to 4, and preferably 1 to 3, hydroxy  
20 groups. Suitable hydroxyaromatic compounds include phenol,  
21 catechol, resorcinol, hydroquinone, pyrogallol, and the  
22 like. The preferred hydroxyaromatic compound is phenol.

23

24 The polyisobutene employed in the process of the present  
25 invention is a polyisobutene having a high methylvinylidene  
26 isomer content, that is, at least about 70%  
27 methylvinylidene. Suitable high methylvinylidene  
28 polyisobutenes include those prepared using boron  
29 trifluoride catalysts. The preparation of such  
30 polyisobutenes in which the methylvinylidene isomer  
31 comprises a high percentage of the total olefin composition  
32 is described in U.S. patent Nos. 4,152,499 and 4,605,808,  
33 the disclosures of each of which are incorporated herein by  
34 reference.

- 5 -

01 The polyisobutene contemplated for use in the present  
02 invention will have a number average molecular weight in the  
03 range of about 300 to 5,000, preferably in the range of  
04 about 400 to 3,000, and more preferably in the range of  
05 about 500 to 2,000.

06

07 Examples of suitable polyisobutenes having a high  
08 methylvinylidene content include Ultravis 10, a  
09 polyisobutene having a molecular weight of about 950 and a  
10 methylvinylidene content of about 76%, and Ultravis 30, a  
11 polyisobutene having a molecular weight of about 1300 and a  
12 methylvinylidene content of about 74%, both available from  
13 British Petroleum.

14

15 The catalyst employed in the process of the present  
16 invention will generally be any of the well known acidic  
17 alkylation catalysts. Typical acidic alkylation catalysts  
18 include Lewis acids, trifluoromethanesulfonic acid, and  
19 acidic molecular sieve catalysts. Suitable Lewis acids  
20 include aluminum trichloride, boron trifluoride and boron  
21 trifluoride complexes, such as boron trifluoride etherate,  
22 boron trifluoride-phenol and boron trifluoride-phosphoric  
23 acid. Typical molecular sieve type catalysts include  
24 Amberlyst 36, available from Rohm and Haas, Philadelphia,  
25 Pennsylvania. Preferred acidic alkylation catalysts include  
26 trifluoromethanesulfonic acid, boron trifluoride and boron  
27 trifluoride complexes. In general, the stronger acidic  
28 alkylation catalysts will be employed with higher molecular  
29 weight polyisobutenes.

30

31 Typically, the reaction temperature for the alkylation  
32 reaction will be in the range of about 0°C to 100°C, and  
33 preferably in the range of about 20°C to 60°C. The reaction

34

-6-

01 pressure will generally be atmospheric, although higher or  
02 lower pressures may be employed.

03

04 The molar ratio of the hydroxyaromatic compound to  
05 polyisobutene is normally in the range of about 1.2:1 to  
06 5:1, and preferably will be in the range of about 2:1 to  
07 3:1. In general, the number of equivalents of the acidic  
08 alkylation catalyst per equivalent of polyisobutene will be  
09 in the range of about 0.005:1 to 5:1, and preferably in the  
10 range of about 0.05:1 to 0.6:1.

11

12 The alkylation reaction may be carried out neat or in the  
13 presence of a solvent which is inert to the reaction of the  
14 hydroxyaromatic compound and the polyisobutene. When  
15 employed, a typical solvent is hexane.

16

17 The alkylation reaction will generally be carried out over a  
18 period of about 2 to 48 hours, and preferably over a period  
19 of about 3 to 20 hours. Upon completion of the reaction,  
20 the desired polyisobutyl hydroxyaromatic compound is  
21 isolated using conventional techniques.

22

23 The following examples are presented to illustrate specific  
24 embodiments of this invention and are not to be construed in  
25 any way as limiting the scope of the invention.

26

## 27 EXAMPLES

28

### 29 Example 1

30

#### 31 Preparation of Polyisobutyl Phenol

32

33 To a flask equipped with a magnetic stirrer, reflux  
34 condenser, thermometer, addition funnel and nitrogen inlet



- 7 -

01 was added 203.2 grams of phenol. The phenol was warmed to  
02 40°C and the heat source was removed. Then,  
03 73.5 milliliters of boron trifluoride etherate was added  
04 dropwise. 1040 grams of Ultravis 10 polyisobutene  
05 (molecular weight 950, 76% methylvinylidene, available from  
06 British Petroleum) was dissolved in 1,863 milliliters of  
07 hexane. The polyisobutene was added to the reaction at a  
08 rate to maintain the temperature between 22-27°C. The  
09 reaction mixture was stirred for 16 hours at room  
10 temperature. Then, 400 milliliters of concentrated ammonium  
11 hydroxide was added followed by 2,000 milliliters of hexane.  
12 The reaction mixture was washed with water (3 x 2,000  
13 milliliters), dried over magnesium sulfate, filtered and the  
14 solvents removed under vacuum to yield 1,056.5 grams of a  
15 crude reaction product. The crude reaction product was  
16 determined to contain 80% of the desired product by proton  
17 NMR and chromatography on silica gel eluting with hexane,  
18 followed by hexane: ethylacetate: ethanol (93:5:2).

19

20

Example 2

21

22 Various alkylation reactions were carried out in accordance  
23 with the process of the present invention, using  
24 polyisobutenes having a high methylvinylidene isomer  
25 content. These reactions were compared with alkylation  
26 reactions employing conventional polyisobutenes having only  
27 minor amounts of methylvinylidene isomer present.

28

29 The polyisobutenes employed in the alkylation reactions  
30 demonstrating the present invention were Ultravis 10  
31 polybutene having a number average molecular weight of about  
32 950 and a methylvinylidene isomer content of about 76% and  
33 Ultravis 30 polyisobutene having a number average molecular  
34 weight of about 1300 and a methylvinylidene isomer content

01 of about 74%, both of which are commercially available from  
02 British Petroleum. The polyisobutenes employed for  
03 comparison purposes were Parapol 950 polyisobutene having a  
04 number average molecular weight of about 950 and a  
05 methylvinylidene isomer content of about 2% and Parapol 1300  
06 polyisobutene having a number average molecular weight of  
07 about 1300 and a methylvinylidene isomer content of about  
08 6%, both available from Exxon Chemical Company.

09

10 Each of the alkylation reactions were carried out using  
11 2 equivalents of phenol as the hydroxyaromatic compound and  
12 1 equivalent of polyisobutene. The reactions were carried  
13 out over a period of about 15 hours.

14

15 The results are shown in Table 1. These results show that  
16 the alkylation reactions of the present invention employing  
17 high methylvinylidene polyisobutene provided the desired  
18 polyisobutyl phenol in significantly higher yield than the  
19 alkylation reactions employing conventional polyisobutene  
20 having minor amounts of methylvinylidene. In addition, the  
21 polyisobutyl phenols prepared in accordance with the present  
22 invention exhibited minimal molecular weight degradation.  
23 Moreover, the polyisobutyl phenols produced pursuant to the  
24 present invention contained an average of about 70% to 100%  
25 para-substitution. This compares to an average of about 0%  
26 to 40% para-substitution for the polyisobutyl phenols  
27 prepared with the conventional low vinylidene  
28 polyisobutenes. Para-substituted polyisobutyl phenols are  
29 preferable for a number of uses. For example, when  
30 polyisobutyl phenols are employed as fuel additives,  
31 para-substitution generally provides enhanced fuel additive  
32 performance.

33

34

TABLE 1

Run No.	Polyisobutene	Acidic Catalyst	Mole Equiv. (Catalyst)	Temperature, °C	Yield	Mol. Wgt. (VPO) <sup>a</sup>	Mol. Wgt. (PMR) <sup>b</sup>
1	Parapol 950	CF <sub>3</sub> SO <sub>3</sub> H	.05 (0.8 wt. %)	Room Temp. <sup>c</sup>	61%	1069	1162
2	Ultravis 10	CF <sub>3</sub> SO <sub>3</sub> H	.05	Room Temp. <sup>c</sup>	91%	1114	1106
3	Parapol 950	BF <sub>3</sub> • Et <sub>2</sub> O	.55	Room Temp. <sup>c</sup>	15%	604	656
4	Ultravis 10	BF <sub>3</sub> • Et <sub>2</sub> O	.55	Room Temp. <sup>c</sup>	80%	1197	1218
5	Parapol 950	BF <sub>3</sub> • H <sub>3</sub> PO <sub>4</sub>	.55	Room Temp. <sup>c</sup>	11%	533	600
6	Ultravis 10	BF <sub>3</sub> • H <sub>3</sub> PO <sub>4</sub>	.55	Room Temp. <sup>c</sup>	83%	1162	1162
7	Parapol 950	BF <sub>3</sub> • phenol	.55	Room Temp. <sup>c</sup>	90%	656	656
8	Ultravis 10	BF <sub>3</sub> • phenol	.05	45° C. <sup>d</sup>	82%	994	994
9	Parapol 1300	CF <sub>3</sub> SO <sub>3</sub> H	.05	Room Temp. <sup>c</sup>	14%	1088	994
10	Ultravis 30	CF <sub>3</sub> SO <sub>3</sub> H	.05	Room Temp. <sup>c</sup>	71%	1521	1386

a VPO = vapor pressure osmometry

b PMR = proton magnetic resonance

c Room Temperature was approximately 23°C.

d Reaction time was 5 hours.

PR3032

-10-

01 WHAT IS CLAIMED IS:

02

03 1. A process for the preparation of a polyisobutyl  
04 hydroxyaromatic compound which comprises alkylating a  
05 hydroxyaromatic compound in the presence of an acidic  
06 alkylation catalyst with a polyisobutene having a  
07 number average molecular weight in the range of about  
08 300 to 5,000 and wherein the polyisobutene contains at  
09 least about 70% of a methylvinylidene isomer.

10

11 2. The process according to Claim 1, wherein the  
12 hydroxyaromatic compound is phenol.

13

14 3. The process according to Claim 1, wherein the  
15 polyisobutene has a number average molecular weight of  
16 about 400 to 3,000.

17

18 4. The process according to Claim 3, wherein the  
19 polyisobutene has a number average molecular weight of  
20 about 500 to 2,000.

21

22 5. The process according to Claim 1, wherein the acidic  
23 alkylation catalyst is selected from the group  
24 consisting of a Lewis acid, trifluoromethane sulfonic  
25 acid and an acidic molecular sieve.

26

27 6. The process according to Claim 5, wherein the acidic  
28 alkylation catalyst is a Lewis acid.

29

30 7. The process according to Claim 6, wherein the Lewis  
31 acid is boron trifluoride or a boron trifluoride  
32 complex.

33

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-11-

- 01 8. The process according to Claim 5, wherein the acidic  
02 alkylation catalyst is trifluoromethane sulfonic acid.  
03
- 04 9. The process according to Claim 1, wherein the  
05 alkylation temperature is in the range of about 0° to  
06 100°C.  
07
- 08 10. The process according to Claim 9, wherein the  
09 alkylation temperature is in the range of about 20° to  
10 60°C.  
11
- 12 11. The process according to Claim 1, wherein the molar  
13 ratio of hydroxyaromatic compound to polyisobutene is  
14 about 1.2:1 to 5:1.  
15
- 16 12. The process according to Claim 11, wherein the molar  
17 ratio of hydroxyaromatic compound to polyisobutene is  
18 about 2:1 to 3:1.  
19
- 20 13. The process according to Claim 1, wherein the number of  
21 equivalents of catalyst per equivalent of polyisobutene  
22 is about 0.005:1 to 5:1.  
23
- 24 14. The process according to Claim 13, wherein the number  
25 of equivalents of catalyst per equivalent of  
26 polyisobutene is about 0.05:1 to 0.6:1.  
27  
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## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US93/12426

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(5) : C07C 37/00, 37/16; C08G 67/02

US CL : 528/392; 568/790, 792, 793

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

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Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A,P	US, A, 5,192,335 (CHERPECK) 09 MARCH 1993.	1-14
A	US, A, 4,605,808 (SAMSON) 12 AUGUST 1986.	1-14
A	US, A, 4,238,628 (CAHILL) 09 DECEMBER 1980.	1-14
A	US, A, 4,231,759 (UDELHOFEN) 04 NOVEMBER 1980.	1-14
A	US, A, 4,152,499 (BOERZEL) 01 MAY 1979.	1-14

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Date of the actual completion of the international search

02 MARCH 1994

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# INTERNATIONAL SEARCH REPORT

International application No.  
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## B. FIELDS SEARCHED

Minimum documentation searched

Classification System: U.S.

C07C 2/34, 9/00, 37/00, 37/16; C08F 4/00, 4/14, 8/32, 10/00; C08G 67/02; C10L 1/16; C10M 105/02; 44/442, 450;  
252/51.5A; 525/381; 526/237, 272, 348.7; 528/392; 568/790, 792, 793; 585/15, 511, 516, 525